

(19) World Intellectual Property Organization
 International Bureau



(43) International Publication Date
 6 November 2003 (06.11.2003)

PCT

(10) International Publication Number
 WO 03/091307 A1

- (51) International Patent Classification: C08G 18/12, 18/72, 18/48, 18/54, C09D 175/04, 11/00
- (74) Agents: HEPP, Dieter et al.; Hepp, Wenger & Ryffel AG, Friedtalweg 5, CH-9500 Wil (CH).
- (21) International Application Number: PCT/EP03/04242
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 22 April 2003 (22.04.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 02009427.2 25 April 2002 (25.04.2002) EP
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant (for all designated States except US): SICPA HOLDING S.A. [CH/CH]; Avenue de Florissant 41, CH-1008 Prilly (CH).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): EUGENE, Denis [FR/FR]; 138 Avenue de la Gare, F-74800 La Roche sur Foron (FR). EISELE, Gilles [FR/FR]; Chez Mermier, F-74250 Fillinges (FR). CATHERIN, Gilles [FR/FR]; Presbytère, 25 Rue de l'Eglise, F-01630 Saint Genis Pouilly (FR).
- Published:
 — with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: A POLYURETHANE RESIN DERIVED FROM POLYHYDROXYLATED RESINS

(57) Abstract: The present invention is related to a polyurethane resin being the reaction product of at least one diisocyanate and a group of components having isocyanate reactive functional groups, said group of components comprising a first group of one or more polyether polyols each having an average molecular weight in the range of between 400 to 12000 g/mol, a second group of one or more polyhydroxylated resins selected from the group consisting of ketonic resins, polyester resins, acrylic-styrene copolymers, acrylic polyols, rosin derivatives and terpene-phenolic resins, optionally a third group of one or more polyols each having an average molecular weight of equal or less than 800 g/mol, and at least one amine and a reaction terminating agent, wherein the ratio of the equivalent weights of the diisocyanate to the components having isocyanate reactive functional groups is selected such that essentially all of the isocyanate groups of the diisocyanate are present as the reaction product with one of said isocyanate reactive functional groups.

WO 03/091307 A1

A polyurethane resin derived from polyhydroxylated resins

The present invention relates to a polyurethane resin, to a coating composition comprising said polyurethane resin, to the use of said polyurethane resin for printing plastic substrates, to a method of producing a polyurethane resin and to a method of producing a laminate carrying a printed image, according to the preamble of the independent claims.

Polyurethane resins are the binders of choice in solvent borne coating compositions for plastic films and in the production of image carrying laminates. Laminates are multi-layered shaped articles in which – according to the needs of the final article – each of the layers consist either of the same or of different materials. The preferred materials are paper, wood, textiles, metal and plastic films. In the field of food packaging, the laminates are mostly made from plastic or metal films, in particular metallized films, or a combination of both. Film materials are chosen such that the laminates can be subjected to sterilization processes without deterioration of the film and/or the laminate. As a further advantage laminates impart to prints or generally images a satisfying appearance with respect to gloss and color fastness. Generally laminates are produced by either joining two or more layers by means of adhesives or by adhesive-free extrusion coating. Irrespective of the production process a print or generally any kind of image which does not necessarily have to be printed can be applied to one or both of the layers prior to applying the next layer (Römpf Lexikon, Lacke und Druckfarben, ed. U.Zorll, Georg Thieme Verlag, Stuttgart, New York 1998, p.214 and 318).

Coating compositions for laminates, which are mainly in the form of printing inks, have to satisfy high standards. The resin as the film forming part of the composition must provide the dried layer with the required adhesive strength both to the underlying substrate and to the adhesive or to the extruded layer. As a further requirement the resin must impart to the dried layer stability during and after sterilization processes and/or treatment in boiling water even over a prolonged period of time (e.g. during food preparation). Further the dried layer must show blocking resistance and stability during sealing of the laminate (e.g. in the production of bags). The composition – as a printing ink – must be printable in flexo and gravure printing processes which are the techniques

commonly used for printing plastic films. Thus, the resin must allow the printing ink to be thinly liquid, rapidly drying and to be soluble in esters and in alcohols, in particular in ethanol.

EP-604 890 teaches a printing ink (for printing laminates) based on a polyurethane resin. The polyurethane resin is the reaction product of a high molecular weight polyol compound of a molecular weight in the range of between 3000 to 10000, a low molecular weight polyol compound of a molecular weight of less than 200, an organic diisocyanate compound, a chain extender and optionally a reaction terminating agent. The polyol compounds are chosen such that the whole of the high molecular weight polyol compound and the low molecular weight polyol compound has an average molecular weight in the range of between 1500 and 2700, the isocyanate index of the diisocyanate being more than 2.0 and the nitrogen content of the polyurethane resin derived from the isocyanate groups of the diisocyanate being from 1.3 to 1.95% by weight. Only standard polyether polyols such as polyethylene glycol are used. Furthermore, the importance of the selected molecular weight range of the polyol component is stressed in that by using a polyol component having a lesser molecular weight an ink having poor adhesiveness and adaptability for boiling or retorting treatment is obtained.

Whereas printed and dried layers produced with the ink of EP-604 890 show in most of the cases the required bond strength, the initial adhesiveness of the layers to the underlying substrate, i.e. the adhesiveness within the first 30 seconds after drying, is poor. A lack of initial adhesiveness results in at least partial transfer of the printed layers to the back side of the substrate/film to which the layer has been applied during storage on rollers or stacks. A further drawback of the prints/layers produced with the ink of EP 604 890 is their lack in heat resistance in particular on coextruded polypropylene and polyester. The latter results in damages on edges of the layers during heat treatment of the laminate. In addition the printing ink shows poor compatibility with alcohols as the solvent of choice in flexographic applications. All these drawbacks are mainly due to lack of performance of the polyurethane resin.

it was the object of the present invention to provide polyurethane resins applicable as film forming binders in coating compositions showing a good initial adhesiveness and a good compatibility with alcohols as well as a good heat resistance, and especially showing good adhesiveness on specific substrates and being harder than common PU resins, so that – in the broadest sense – any kind of dried layers on plastic films and/or laminates can be obtained, said layers having an excellent initial adhesiveness in particular such that the layer is not damaged during storing and further processing of the substrate/film and during finishing of the laminate, in particular that the risk of delamination during sealing of the plastic film or laminate is reduced.

The above object is solved according to the present invention by a polyurethane resin being the reaction product of at least one diisocyanate and a group of components having isocyanate reactive functional groups, said group of components comprising:

- a) a first group of one or more polyether polyols each having an average molecular weight in the range of between 400 to 12000 g/mol,
- b) a second group of one or more polyhydroxylated resins selected from the group consisting of hard ketonic resins, ketonic resins, polyester resins, acrylic-styrene copolymers, acrylic polyols, rosin derivatives and terpene-phenolic resins,
- c) optionally a third group of one or more polyols each having an average molecular weight of equal or less than 800 g/mol, and
- d) at least one amine and a reaction terminating agent,

wherein the ratio of the equivalent weights of the diisocyanate to the components having isocyanate reactive functional groups is selected such that essentially all of the isocyanate groups of the diisocyanate are present as the reaction product with one of said isocyanate reactive functional groups.

The use of a polyhydroxylated resin as one isocyanate reactive component provides PU resins which are harder than commonly used PU resins and which show good adhesiveness on specific substrates such as BOPP (biaxially oriented polypropylene).

According to the present invention, definitions of ranges are intended to include the boundaries of those ranges. For example, a molecular weight range of from 2000 to

3000 g/mol shall also mean to include compounds having an average molecular weight of 2000 g/mol and of 3000 g/mol.

The polyurethane resin of the present invention has a weight average molecular weight of between 3000 and 80.000 g/mol, preferably 20000 to 80000 g/mol, more preferably between 35000 to 55000 g/mol and is soluble in organic solvents which comprise alcohols such as ethanol and ethyl acetate.

In a preferred embodiment the polyurethane resin of the present invention has a urethanisation between 10 to 60%, preferably 10 to 20%.

The favourable properties of the polyurethane resin with regard to its binder qualities in coatings can be influenced by a series of equivalent weight ratios between the reactands. It is to be understood that all the ratios listed hereinafter merely represent embodiments adapted to meet diverse needs of the resin:

According to a preferred embodiment of the present invention, the ratio of the equivalent weights of the diisocyanate to the entirety of the polyether polyols of the first group, of the polyhydroxylated resins of the second group and of the polyols of the third group is in a range of 3.6 : 1 to 1 : 1, preferably 1,5 : 1.

According to another preferred embodiment of the present invention, the ratio of the equivalent weights of the diisocyanate to the components having isocyanate reactive functional groups is preferably in a range of between 0.8:1 to 1.2:1, more preferably of between 0.95:1 to 1.2:1, and even more preferably of between 1:1 to 1.1 :1.

According to another preferred embodiment of the present invention, the ratio of the equivalent weights of the diisocyanate to the amines is in a range of 2:1 to 6:1, preferably in a range of between 3:1 to 6:1, and more preferably in a range of between 3:1 to 5:1.

In a preferred embodiment the diisocyanates are selected from the groups consisting of isophorone-diisocyanate (IPDI), 4,4'- diisocyanato-diphenylmethane (MDI),

hexamethylene-diisocyanate (HMDI) dicyclohexylmethane diisocyanate and toluol-diisocyanate (TDI). In particular the IPDI is either used alone or in a 1 : 1 mixture with MDI. In a further preferred embodiment even polyisocyanate resins are applicable. However, it is to be understood that any diisocyanate commonly used in the synthesis of polyurethane resins can be applied for the purpose of the present invention.

As components having isocyanate reactive functional groups only those components are applied which contain hydroxy and/or amine groups. Although aminoalcohols (compounds containing hydroxy and amine groups) are not excluded from the present invention, pure components, i.e. components which have either hydroxy or amine groups as the only isocyanate reactive functional groups are preferred.

The polyether polyols of the first group are preferably selected from the group consisting of dihydroxy- and trihydroxy polyether polyols having an average molecular weight of from 400 to 12000 g/mol, preferably 400 to 10000 g/mol, more preferably 1000 to 10000 g/mol, and even more preferably 2000 to 6000 g/mol, for example with a hydroxy value in a range of between 18.7 and 56 mg KOH/g. Polyoxyalkylene glycols such as Polypropylene glycol (PPG) or Polytetrahydrofuran (poly(THF)) are the most preferred dihydroxy polyether polyols. Polypropylene glycol (PPG) has worked out to be the most suitable polyoxyalkylene glycol in the synthesis of the polyurethane resin of the present invention. Further preferred as dihydroxy polyether polyol is a polycaprolactone based polyether. However, also polyols based on triols or even higher functional polyols as monomers such as glycerin, trimethylolpropane, pentaerythritol, sorbitol, trimethiolethane or 1,2,3-butanetriol are suitable for the purpose of the present invention.

The polyhydroxylated resins of the second group are selected from the group consisting of hard ketonic resins, ketonic resins, polyester resins, acrylic-styrene copolymers, acrylic polyols, rosin derivatives and terpene-phenolic resins.

According to the present invention, the hard ketonic resins have preferably a hydroxy value of at least 100mg KOH/g but not more than 500mg KOH/g. In particular, a hard ketonic resin which is the hydrogenated condensation product of an aromatic ketone

with an aldehyde, especially the hydrogenated condensation product of acetophenone and formaldehyde is preferred. Such a resin is sold, for example, under the trade name synthetic resin SK from Hüls and has a hydroxyl number of around 325 mg KOH/g. However, according to the present invention, polyhydroxylated resins other than hard ketonic resins are preferred.

According to the present invention, the ketonic resins are preferably polyketonic resins, for example aldehyde-ketone resins such as K-1717 HMP or K-1728 sold by Lawter International Inc, cyclohexanone condensation products having preferably a hydroxyl number of 100-200 KOH/g, for example Laropol K80 sold by BASF, or condensation products of an aliphatic ketone with formaldehyde having preferably a hydroxyl number below 100 KOH/g, such as Synthetic resin TC sold by Degussa-Hüls.

According to the present invention, the polyester resins are preferably unsaturated styrene-free resins having preferably a hydroxyl number below 100 KOH/g, such as Haftharz LTH sold by Hüls.

According to the present invention, the acrylic-styrene copolymers are preferably hydroxy-functional copolymers having preferably a hydroxyl number between 50 and 150 KOH/g, such as NeoCryl B-850 sold by Zeneca.

According to the present invention, the acrylic polyols are resinous polyols having preferably a hydroxyl number between 100 and 200 KOH/g, such as Reactol 180 sold by Lawter International Inc.

According to the present invention, the rosin derivatives are preferably maleic or fumaric rosin derivatives.

According to the present invention, the terpene-phenolic resins preferably have a hydroxyl number between 100 and 200 KOH/g, such as Dertophene H 150 sold by Les Dérivés Résiniques & Terpéniques S.A..

The polyols of the third group are preferably selected from the group consisting of monomeric diols, such as neopentyl glycol, hexane diol or 1,4 butanediol, dihydroxy polyether polyols such as polypropylene glycol, or polyester polyols. The polyester polyols preferably have a hydroxy value of at least 140mg KOH/g. Preferably the polyester polyol is an adipate polyester based polyol.

The amine applied in the synthesis of the polyurethane resin of the present invention is selected from those having an average molecular weight in the range of between 60 to 400g/mol. Preferably the amine is a diamine. The diamine are preferably selected from the group of 1,3 bis (amino ethyl) cyclohexane, m-xylene diamine or isophorone diamine. Isophorone diamine (IPDA) influences the initial adhesion of coatings to some kind of plastic substrates favourably.

The terminating agents are selected from the group consisting of monoethanol amines such as mono-, di-, triethanolamine, ethanol, n-propanol, isopropanol, 1,4- butandiol.

According to the present invention, a polyurethane resin is preferred which is the reaction product of at least one diisocyanate with a group of isocyanate-reactive compounds consisting of at least one of one or more polyether polyols each having an average molecular weight in the range of between 400 to 10000g/mol, preferably 1000 to 10000 g/mol, one or more polyhydroxylated resins selected from the group consisting of ketonic resins, polyester resins, acrylic-styrene copolymers, acrylic polyols, rosin derivatives and terpene-phenolic resins, optionally a third group of one or more polyols each having an average molecular weight of equal or less than 800 g/mol, and at least one amine and a reaction terminating agent, wherein the ratio of the equivalent weights of the diisocyanate to the components having isocyanate reactive functional groups is selected such that essentially all of the isocyanate groups of the diisocyanate are present as the reaction product with one of said isocyanate reactive functional groups.

A particularly preferred polyurethane resin is the reaction product of at least one diisocyanate such as a 1:1 mixture of IPDI and MDI with isocyanate-reactive compounds comprising a polypropylene glycol (PPG) having an average molecular weight of around 4000-4500 g/mol, synthetic resin SK as polyhydroxylated resin, 1,4-

butanediol as low molecular weight polyol, and one or more amine compounds such as IPDA and monoethanolamine.

The polyurethane resin according to the present invention can be synthesized by

- a) first reacting a mixture comprising: a first group of one or more polyether polyols each having an average molecular weight in the range of between 400 to 12000 g/mol, a second group of one or more polyhydroxylated resins selected from the group consisting of hard ketonic resins, ketonic resins, polyester resins, acrylic-styrene copolymers, acrylic polyols, rosin derivatives and terpene-phenolic resins, and optionally a third group of one or more polyols each having an average molecular weight of equal or less than 800 g/mol, with at least one diisocyanate to an isocyanate terminated prepolymer, the ratio of the equivalent weights of the diisocyanate to the entirety of the polyether polyols of the first group, of the polyhydroxylated resins of the second group and of the polyols of the third group is in a range of 3.6 : 1 to 1 : 1, and
- b) in a second step reacting said isocyanate terminated prepolymer with at least one diamine, and
- c) in a third step reacting the product obtained according to step b) with a terminating agent to a saturated polyurethane resin.

Saturated in this context means that the polyurethane resin has essentially no free unreacted isocyanates left.

The conditions under which the starting materials are reacted with each other are the standard methods for synthesizing polyurethane resins and are commonly known to the man skilled in the art.

Further part of the present invention is a coating composition comprising an organic solvent and the polyurethane resin of the present invention as at least one of the film forming binders. In a preferred embodiment the coating composition is a printing ink for printing plastic substrates and for the production of printed laminates. In both the

coating composition and the printing ink, the polyurethane resin can be applied as the sole film forming binder.

The solvent is selected from the group of polar organic solvents, preferably from the group of alcohols and esters.

The polyurethane resin allows the printing ink to be easily adjusted to the needs of flexographic and gravure printing. Such an ink is soluble in alcohols, e.g. in ethanol, has a low viscosity, thus is thinly liquid, with a viscosity preferably between 30 to 100 seconds in a Cup 4 at 23°C or 80 to 350 mPa's at 23°C.

Depending on the chemical structure of the polyurethane resin and thus on the chemical nature of the reactands and their respective ratios to each other the printing inks are adjustable to the needs of different kinds of plastic substrates and/or application methods.

In the context of the present invention the following definitions are given:

- The molecular weights are expressed as weight average molecular weights.
- The average molecular weight of sum of the polyols of the first, second, and third group is calculated

$$i, x=3$$

$$\sum (Mw_{ix} \cdot w_{ix})$$

$$i, x=1$$

Mw_{ix} = molecular weight of polyol i in group x, wherein x= 1-3

w_{ix} = mol fraction of polyol i in group x, wherein x= 1-3

The term "film forming" is defined according to DIN 55945: 1996-09. Film forming is the generic term for the transition of a coating layer from the liquid to the solid state. Film forming occurs by means of physical drying and/or curing. Both processes proceed

simultaneously or one after the other. The polyurethane resin of the present invention is film forming under standard conditions (25°C, minimum 40% relative humidity). Whereas the term "drying" is more related to the process engineering used for drying the liquid layer, such as ovens and temperatures, the term "curing" is related to the chemical processes within the resin during the drying process. The polyurethane of the present invention is of the non-crosslinking type.

"Initial adhesion" is defined as being the adhesion immediately after drying and up to 30 seconds maximum after drying of the layer.

"Drying" means substantial removal of the solvent from the layer. The latter is one of the requirement that the layer becomes solid. The residual solvent in the layer is not more than 10% by weight of the weight of the overall solvent. A dried layer is a layer of a thickness between 4 and 6 μm in particular 5 μm after treatment in an IR-oven by 70 - 80°C for less than one minute. In the solid state the layer is tack-free. In case the layer is thicker or thinner either the oven temperature has to be increased/decreased or the duration of heat treatment has to be adapted correspondingly.

"Layer" and "image" are used synonymously throughout the specification. Layers and images are in form of pictures, writings, overprints, (overprint varnishes) and their meaning should not be limited by their form, extension and thickness.

In the context of the present invention all technical terms shall be defined according to Römpp Lexikon, ed. U.Zoll, Georg Thieme Verlag Stuttgart, 1998.

The present invention further encompasses a method of producing a laminate carrying a printed image, said method comprises the step of

- a) providing a printing ink comprising at least one organic solvent and at least one polyurethane resin of the present invention as at least one film forming binder and
- b) applying a layer to a first substrate by printing said printing ink provided in step (a) in a flexographic and/or gravure printing process to said first substrate

- c) removing said solvent from said layer applied in step (b) thereby drying and/or curing the layer
- d) applying an adhesive to the layer of step (c) and finishing the laminate by applying a second substrate on the adhesive.

Preferably, the first and the second substrates are of a plastic material, preferably of polyolefinic nature. The first and the second substrate can also be of different chemical nature like polyester or polyamide.

According to the present invention, as an adhesive in this process can be used any conventional solvent-free adhesive or solvent-based adhesive. Examples for solvent-based adhesives to be used according to the present invention are Adcote 545/CAT F and Morton 301A/350A from Rohm&Haas, Novacote 275A/CA12 or Novacote 120 ASL/111B from Novacote Flexpack, and Henkel UK 3640/UK 6800 from Henkel. An example for a solvent-free adhesive to be used according to the present invention is Mor-free SK403/C83 from Rohm&Haas.

The adhesives are applied to the layer according to conventional methods, for example by using a hand coater. Solvent-free adhesives are preferably diluted with a conventional diluent such as ethyl acetate before application. Preferably, a solution containing 20 % by weight to 80 by weight, more preferably 30 by weight to 60 by weight of the solvent-free adhesive is prepared hereby.

In the case of solvent-based adhesives, it is preferred according to the present invention to apply said adhesive to the printed layer of a substrate, and then to finish the laminate by applying a second substrate on the adhesive. In the case of a solvent-free adhesive, however, it is more preferred to apply said adhesive to an unprinted layer of a substrate, and then to finish the laminate by applying the printed layer of a second substrate to the adhesive.

Further part of the present invention is therefore a laminate produced by the method mentioned hereinbefore. Of course, the laminate can also be produced by extruding the

second substrate on the first substrate carrying the dried layer. This method does not call for an adhesive.

If necessary, the ink composition of the present invention can contain additional binder resins, e.g. cellulosic resins, acrylic resins, polyvinyl chloride.

The present invention will be described in more detail by the following examples. Unless otherwise indicated, all percentages are % by weight. Eq stands for equivalents.

General synthesis of the polyurethane resin

A five-neck flask equipped with two additions funnels, a gas introduction means, an agitator and a thermometer was charged with a mixture of 60% ethyl acetate and 0.06% Irganox 1076. The mixture was thermostated at 25°C at an agitation velocity of 60 rpm and an nitrogen stream of 0.4 m³/h. The temperature was increased to 60°C and a mixture of 6,59% (1,5 Eq) IPDI, 7,45% (1,5 Eq) of Desmodur 2460M (MDI) and 0.03% DBTDL (catalysator) diluted in 0.03% ethyl acetate was added to the flask. The agitation velocity was increased to 90 rpm. To the isocyanate solution 77,77% (1 Eq) Acclaim 4200 (a polypropyleneglycol sold by Bayer) was added over a period of 10 minutes. The reaction was conducted by a temperature of 74°C for 180 minutes. Then, 3,64% (0,37 Eq) Reactol 180 was slowly added to the prepolymer solution, and the reaction was conducted for 15-30 minutes. Thereafter, 2,73% (0,84 Eq) isophorone diamine was added at an agitation velocity of 120 rpm. The reaction was conducted for another 15 minutes. Then, 0,82% (0,47 Eq) 1,4-Butanediol was added for another 15-30 minutes. Thereafter, 1% (0,43 Eq) monoethanolamine was added to the prepolymer solution. After a reaction time of 15 minutes, 10% of ethanol was added for dilution.

The resulting polyurethane resin had a dry content of 30%, a viscosity of 15 P at 25°C, and an urethanisation degree of 15%.

The NCO-values are determined after each step and the increase in molecular weight of the polyurethane during synthesis is observed by GPC measurements (Pump : Waters 515 HPLC; Injection : Waters 717 plus autosampler, Detector : Waters 2414 refractive

index; Columns : styragel HR1 (100 - 5000), styragel HR4E (50-100000); Standard calibration Polystyrene : 381 : 478 : 2950 : 6520 : 9650 : 18600 : 43700 : 177000 : 387000).

Method of measurement the initial adhesion:

A self adhesive tape (10 cm, type 683 of 3M) is applied under uniform pressure onto a printed layer immediately after drying of the layer and torn off the substrate immediately thereafter. The quantity of the print adhered to the tape is classified on a scale from 0 to 5 wherein 0 means more than 95% of the printed layer adhered to the tape, 1 means more than 50% of the printed layer adhered to the tape, 2 means less than 30% of the printed layer adhered to the tape; 3 means less than 20% of the printed layer adhered to the tape, 4 means less than 10% of the printed layer adhered to the tape and 5 is less than 2% of the printed layer adhered to the tape. The test results is executed additionally in dependence of the drying time of the printed layer.

Formulation of printing ink comprising the polyurethane resins according to the present invention

Formulation of the technologic varnish based on the PU :

Polyurethane resin	70 parts per weight
Inert resin	11 parts per weight
Nitrocellulose	2 parts per weight
Inert resin	6 parts per weight
Adhesion promoter	8 parts per weight
Wax	3 parts per weight

Formulation of a White printing ink :

white paste	46 parts per weight
ethyl acetate	4.5 parts per weight
n-propanol	5 parts per weight
Technologic varnish	38 parts per weight
Nitrocellulose	6.5 parts per weight

Formulation of a Blue printing ink :

blue paste	50 parts per weight
ethyl acetate	4 parts per weight
n-propanol	4 parts per weight
Technologic varnish	38 parts per weight
Nitrocellulose	4 parts per weight

Initial adhesion, heat resistance and laminations/delamination strength are tested on substrates of different chemical nature and are compared to the corresponding results of a printing ink formulated from a polyurethane resin which was synthesized without a hydrophilic, water-soluble polyol component.

The following substrates were used:

<u>Product name</u>	<u>Chemical nature</u>	<u>Producer</u>
MB 200	coextruded bi-oriented polypropylene	Mobil
BOPP chine	biaxially oriented polypropylene	Wu Xi

The initial adhesion and heat resistance are tested on basis of a layer of the printing ink to an underlying substrate. For the lamination/delamination test the bond strength is tested on basis of a layer of the printing ink between two plastic films. The counter substrate for all of the substrates tested is a low density polyethylene film.

Tested are: a print of the white ink as the only layer between the two plastic films, (indicated as white), a print of the cyan ink as the only layer between the two films (indicated as cyan) and a superposition of a layer of the cyan and white ink between the two films (indicated as 200%).

The technique for the production of the laminate is the adhesive based lamination technique. A printed sample of laminate having a width of 15 mm is placed between two jaws of a (dynamometer type Lhomargy). The sample is drawn out and the substrate separated from the counter-substrate. The bond strength (g/15 mm) and the delamination aspect of the tested laminate is evaluated at a speed of 200 mm/min. The bond strength is expressed as a combination of number value and letters. The number value stands for grams needed to separate the laminate of a width of 15 mm and a dynamometer speed of 200mm/min. The higher the value the greater the bond strength. The letters indicate the kind of breakage with regard to the layer of the printing ink:

- T: Transfer of 100% of the ink layer (from the substrate to the counter substrate).
- P: Splitting of the ink layer (between substrate and counter substrate).
- Z: No stable value for the bond strength.
- R: Break/tear of one of the two films of the laminate.

Claims

1. A polyurethane resin being the reaction product of at least one diisocyanate and a group of components having isocyanate reactive functional groups, said group of components comprising:
 - a) a first group of one or more polyether polyols each having an average molecular weight in the range of between 400 to 12000 g/mol,
 - b) a second group of one or more polyhydroxylated resins selected from the group consisting of hard ketonic resins, ketonic resins, polyester resins, acrylic-styrene copolymers, acrylic polyols, rosin derivatives and terpene-phenolic resins,
 - c) optionally a third group of one or more polyols each having an average molecular weight of equal or less than 800 g/mol, and
 - d) at least one amine and a reaction terminating agent,wherein the ratio of the equivalent weights of the diisocyanate to the components having isocyanate reactive functional groups is selected such that essentially all of the isocyanate groups of the diisocyanate are present as the reaction product with one of said isocyanate reactive functional groups.
2. A polyurethane resin according to claim 1 wherein the ratio of the equivalent weights of the diisocyanate to the entirety of the polyether polyols of the first group, of the polyhydroxylated resins of the second group and of the polyols of the third group is in a range of 3.6:1 to 1:1, preferably 1.5:1.
3. A polyurethane resin according to any one of the claims 1 or 2, wherein the ratio of the equivalent weights of the diisocyanate to the components having isocyanate reactive functional groups is preferably in a range of between 0.8:1 to 1.2:1, more preferably of between 0.95:1 to 1.2:1, and even more preferably of between 1:1 to 1.1:1.
4. A polyurethane resin according to any one of the claims 1 to 3, wherein the ratio of the equivalent weights of the diisocyanate to the amines is in a range of 2:1 to

6:1, preferably in a range of between 3:1 to 6:1, and more preferably in a range of between 3:1 to 5:1.

5. A polyurethane resin according to any one of the claim 1 to 4, wherein the polyether polyols of the first group have an average molecular weight in the range of from 2000 to 6000g/mol.
6. A polyurethane resin according to claim 5, wherein the polyether polyols of the first group are selected from the group consisting of dihydroxy and trihydroxy polyether polyols.
7. A polyurethane resin according to claim 6, wherein the dihydroxy polyether polyol is selected from the group consisting of polyoxyalkylene glycol, preferably a polypropyleneglycol or a polytetrahydrofuran, and a caprolactone based polyether.
8. A polyurethane resin according to any one of the claim 1 to 7, wherein the ketonic resins are polyketonic resins, for example aldehyde-ketone resins, cyclohexanone condensation products having preferably a hydroxyl number of 100-200 KOH/g, or condensation products of an aliphatic ketone with formaldehyde having preferably a hydroxyl number below 100 KOH/g.
9. A polyurethane resin according to any one of the claim 1 to 7, wherein the polyester resins are unsaturated styrene-free resins having preferably a hydroxyl number below 100 KOH/g.
10. A polyurethane resin according to any one of the claim 1 to 7, wherein the acrylic-styrene copolymers are hydroxy-functional copolymers having preferably a hydroxyl number between 50 and 150 KOH/g.
11. A polyurethane resin according to any one of the claim 1 to 7, wherein the acrylic polyols are resinous polyols having a hydroxyl number between 100 and 200 KOH/g.

12. A polyurethane resin according to any one of the claim 1 to 7, wherein the terpene-phenolic resins have a hydroxyl number between 100 and 200 KOH/g.
13. A polyurethane resin according to any one of the claims 1 to 12, wherein the polyols of the third group are selected from the group consisting of monomeric diols, dihydroxy polyether polyols, polyester polyols and hard ketonic resin, wherein the hydroxy value of the hard ketonic resin is preferably in a range of between 100 mg KOH/g to 500 mg KOH/g and the hydroxy value of the polyester polyol is at least 140 mg KOH/g.
14. A polyurethane resin according to any one of the claims 1 to 13, wherein the amine is a diamine, preferably selected from the group consisting of isophoronediamine, m-xylene, 1,3 bis (aminoethyl) cyclohexane.
15. Process for preparing a polyurethane resin according to any one of claims 1 to 14, said process comprising the steps of:
 - a) first reacting a mixture comprising: a first group of one or more polyether polyols each having an average molecular weight in the range of between 400 to 12000 g/mol, a second group of one or more polyhydroxylated resins selected from the group consisting of hard ketonic resins, ketonic resins, polyester resins, acrylic-styrene copolymers, acrylic polyols, rosin derivatives and terpene-phenolic resins, and optionally a third group of one or more polyols each having an average molecular weight of equal or less than 800 g/mol, with at least one diisocyanate to an isocyanate terminated prepolymer, the ratio of the equivalent weights of the diisocyanate to the entirety of the polyether polyols of the first group, of the polyhydroxylated resins of the second group and of the polyols of the third group is in a range of 3.6 : 1 to 1 : 1, and
 - b) in a second step reacting said isocyanate terminated prepolymer with at least one diamine, and
 - c) in a third step reacting the product obtained according to step b) with a terminating agent to a saturated polyurethane resin.

16. Polyurethane resin, obtainable by the process according to claim 15.
17. A coating composition, preferably printing ink, comprising a solvent and at least one polyurethane resin according to one of the claims 1 to 14 or 16 as film forming binder.
18. Use of a polyurethane resin according to claims 1 to 14 or 16 as at least one film forming binder in printing inks for printing plastic substrates, preferably polyolefinic plastic substrate.
19. Method of producing a laminate carrying a printed layer, said method comprises the steps of
 - a) providing a coating composition, preferably a printing ink, according to claim 17;
 - b) applying a layer to a first substrate, preferably a plastic foil, by printing said printing ink of step a) in a flexographic and/or gravure printing process;
 - c) removing said solvent from said layer thereby drying and/or curing said layer obtained in step b),
 - d) applying an adhesive to the dried and/or cured layer obtained in step c) and producing the laminate by applying at least a second substrate, preferably a plastic foil, on the adhesive.
20. Laminate produced by the method of claim 19.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 03/04242

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08G18/12 C08G18/72 C08G18/48 C08G18/54 C09D175/04
 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 604 890 A (SAKATA INX CORP) 6 July 1994 (1994-07-06)	1-20
Y	page 4, line 39 - line 42 page 5, line 8 - line 13 page 4, line 57 - line 58	1-20
X	WO 01 14442 A (COGNIS CORP) 1 March 2001 (2001-03-01)	1-20
Y	page 5, line 1 - page 6, line 12; claims 1, 5, 7, 13, 19-21, 26, 35 example 21	1-20
P, X	EP 1 229 090 A (SICPA HOLDING SA) 7 August 2002 (2002-08-07)	1-20
	page 3, line 57 - page 4, line 33; claims 1, 13-15 cited amended claims 1, 13-15 at pages 16-17	
	--- -/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the International filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the International filing date but later than the priority date claimed

"I" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search

14 July 2003

Date of mailing of the international search report

30/07/2003

Name and mailing address of the ISA
 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2200 HV Rijswijk
 Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+31-70) 340-3016

Authorized officer

Scheuer, S

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 03/04242

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 107 097 A (FULLER H B GMBH) 2 May 1984 (1984-05-02) claims 1-7	1-20
X	US 5 700 867 A (IIBUCHI KOUICHI ET AL) 23 December 1997 (1997-12-23) example 1	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/EP 03/04242

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0604890	A	06-07-1994	JP 6248051 A 06-09-1994
			DE 69317996 D1 20-05-1998
			DE 69317996 T2 03-09-1998
			EP 0604890 A1 06-07-1994
			ES 2115002 T3 16-06-1998
			US 5556925 A 17-09-1996
WO 0114442	A	01-03-2001	AU 6777400 A 19-03-2001
			BR 0013434 A 30-04-2002
			EP 1208127 A1 29-05-2002
			WO 0114442 A1 01-03-2001
EP 1229090	A	07-08-2002	EP 1229090 A1 07-08-2002
			DE 60100208 D1 28-05-2003
			WO 02070614 A1 12-09-2002
			US 2002156227 A1 24-10-2002
EP 0107097	A	02-05-1984	DE 3236313 A1 05-04-1984
			AT 28083 T 15-07-1987
			DE 3372293 D1 06-08-1987
			DK 449083 A ,B, 31-03-1984
			EP 0107097 A1 02-05-1984
			ES 8507596 A1 16-12-1985
			FI 833510 A ,B, 31-03-1984
			NO 833545 A ,B, 02-04-1984
US 5700867	A	23-12-1997	JP 2657203 B2 24-09-1997
			JP 7102204 A 18-04-1995
			AU 688785 B2 19-03-1998
			AU 7439394 A 13-04-1995
			DE 69426719 D1 29-03-2001
			DE 69426719 T2 07-06-2001
			EP 0646609 A1 05-04-1995